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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

A NEW INVESTIGATION CONCERNING THE ATOMIC WEIGHT OF URANIUM.

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By Theodore William Richards and Benjamin Shores Merigold.

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Introduction.

Our knowledge of uranium dates from the year 1789, when it was first recognized as an element by Klaproth. It can by no means, therefore, be classed with the new elements, nor is it of great rarity. Nevertheless, comparatively few determinations of the atomic weight of this element have been made, and of these, one only has been carried out with the degree of accuracy necessary in work of this kind. During the fifty years following the discovery of uranium a number of atomic weight determinations were made by Berzelius, Arfvedson, Schönberg, Marchand, and Rammelsberg. This early work is now of historical interest only, for the results vary widely, and in some cases are of such a nature as scarcely to be considered quantitative, in the modern sense of the word. For example, Rammelsberg obtained results varying from 184 to 234, calculated upon the modern basis.

In 1841 Peligot discovered that the substance then known as uranium was not an element, but an oxide. This discovery, while it did not impair the value of the analytical work previously done, necessitated a recalculation of the numerical value of the atomic weight. The new value was 120, and this remained practically unchanged during the next thirty years. When the periodic classification of the elements was first suggested, uranium, with the atomic weight 120, was one of the elements for which there was no place. From a study of the properties of uranium and its compounds, Mendeléeff declared that the atomic weight

* The greater part of the work described in this paper was presented to the Faculty of Arts and Sciences of Harvard University by B. S. Merigold, as a thesis for the degree of Ph.D., in June, 1901.

of uranium was probably 240 instead of 120.* The question was not definitely settled until Zimmermann, in 1885, carried out the suggestions of Mendeléeff, and by specific heat and vapor density determinations confirmed the higher value.†

Owing to the wide variations in the published results, the atomic weight of uranium has long been considered one of the least satisfactorily determined of the atomic weight values. A glance at the results thus far obtained is sufficient to show the need for further work in this line. A complete résumé of the older work upon the subject is to be found in Clarke's recent work on the atomic weights. ‡ The following table summarizes those investigations which seem to possess even a little quantitative value: —

LESS INACCURATE PREVIOUS WORK ON THE ATOMIC WEIGHT OF URANIUM.

O = 16.000

1841	Péligot §— Analysis of Green Chloride	240.±
1842	Ebelmen ‖ — Combustion of Oxalate	238.±
1843	Wertheim ¶ — Double Acetate of Sodium and Uranium	239.±
1846	Péligot ** — Combustion of Oxalate and Acetate . .	240.±
1886	Zimmermann †† — Reduction of Oxide, U_3O_8 to UO_2 .	239.6
1886	Zimmermann ‡‡ — Ignition of Double Acetate . . .	239.5

The work of Ebelmen, Wertheim, and the early work of Péligot is necessarily of little weight in assigning a probable value to the atomic weight of uranium. In some cases the material used was impure, and in others the methods of analysis were faulty. Consequently it is not surprising to find differences of whole units in the individual determinations of each series.

Péligot's later determinations from the oxalate is perhaps the best of the early work. His material was carefully purified, and his method is far preferable to the work of Ebelmen and Wertheim. By combustion

* Annalen der Chemie u. Pharmacie, Supp. Vol. **8**, 178 et. seq.

† Annalen der Chemie u. Pharmacie, **216**, 1.

‡ A Recalculation of the Atomic Weights, by F. W. Clarke, Smithson. Misc. Coll., Constants of Nature, Part V. (1897), 263.

§ Compt. Rend. **12**, 735. Ann. Chim. Phys. (3) **5**, 5 (1842).

‖ J. prkt. Chem. **27**, 385 (1842).

¶ Ibid., **29**, 209 (1843).

** Compt. Rend., **22**, 487 (1846).

†† Ann. d. Chem., **232**, 299 (1886).

‡‡ Ibid.

analysis he determined the ratio between uranium oxide and carbon dioxide. Thus he eliminated the error involved in weighing a crystallized salt which would probably contain more or less included water. The principal sources of error are the questionable use of combustion analysis in atomic weight investigations, and the possibility of unoxidized carbon remaining in the uranium oxide. His best results vary from 239.4 to 241.1.

The work of these chemists, though a great improvement over the attempts of Rammelsberg and the other early workers, leaves much to be desired, and does little more than give an approximate idea of the probable value of the atomic weight of uranium.

Zimmermann's investigation of the ratio between the oxides UO_2 and U_3O_8 was much more carefully carried out, and is the only work thus far published that is worthy of serious consideration. Using carefully purified material, and giving attention to detail, Zimmermann oxidized the lower oxide by means of a stream of oxygen, and observed the gain in weight. His results for the atomic weight varied from 239.49 to 239.76, an extreme difference of 0.27, or 0.11 per cent. The average was about 239.6. The chief probable cause of error in this method is the difficulty which is always experienced in forming a more voluminous solid from a less voluminous one. Uranous oxide has a specific gravity of 10.2, while the "Uranoso-uranic" oxide has a specific gravity of only 7.3. The great increase of volume which occurs when the higher oxide is formed must tend to protect particles of the lower oxide from the action of the oxygen. Hence the gain in weight will be too small, and the apparent atomic weight of the metal too large.* It is clear that a very small deficiency in the weight of the higher oxide must cause a great increase in the apparent atomic weight.

Moreover, any incompleteness in the reduction by which the lower oxide was prepared, or any retention or occlusion of gases within this oxide, would also tend to raise the apparent atomic weight. Hence one is inclined to believe, even without further evidence, that Zimmermann's result for uranium must be too high.

A new determination of the atomic weight of uranium has recently been made by J. Aloy.† The method employed differs materially from any previously used in uranium work. The values obtained are derived

* Compare Richards and Baxter, These Proceedings **34**, 351 (1898). Ztsch. anorg. Chem. **21**, 251 (1899).

† Comptes Rendus, **132**, 551 (1901). This work is discussed rather fully here, since it is too recent to have been included in Clarke's book.

from the ratio between the weight of nitrogen and that of uranous oxide contained in crystallized uranyl nitrate. Uranyl nitrate was purified by repeated crystallization. A quantity of the pure nitrate, the weight of which need not be known, was put into a boat, and the boat surrounded by a section of platinum tube, to prevent loss of material. The whole was placed in a combustion tube between spirals of reduced copper. One end of the combustion tube was connected with a carbon dioxide generator, and the other with an absorption apparatus containing a concentrated solution of potash.

After sweeping the air out of the apparatus with a current of carbon dioxide, the nitrate was heated so long as evolution of nitrogen occurred, the temperature being finally raised to red heat. The reduced copper was kept at red heat throughout the operation. When it was certain that no more nitrogen was evolved, the green oxide remaining in the boat was reduced by hydrogen to uranous oxide and weighed. The nitrogen was transferred to a measuring tube reading to tenths of a cubic centimeter. From the ratio of the weight of this volume of nitrogen to the weight of the oxide, the atomic weight is calculated.

The following are the results of the eight determinations given: —

Atomic Weight of Uranium.

N = 14.04

Volume of nitrogen, 15.25 cc.	33.5	38.0	52.5	81.25	125.0	151.2	165.0
Atomic wt. of uranium, 239.3	239.4	239.6	239.5	239.4	239.5	239.4	239.4
Average							239.4

This method has the merit of simplicity, and does not involve the weight of the crystallized salt. There are, however, several sources of possible constant error that have not been taken into account. When crystallized uranium nitrate is heated, it first melts in its water of crystallization. As in all similar cases, it requires the very greatest care to prevent spattering while the crystal water is being driven off. It was undoubtedly as a precaution against loss of material in this way that Aloy used his platinum tube. By the time the crystal water is expelled, the fused mass has hardened into a solid cake, changing in color from yellow to orange, and finally to the green of urano-uranic oxide, U_3O_8.

This method of preparing the green oxide from pure uranyl nitrate

was used in the work to be described in the following pages. It was *invariably* found, however, that during the decomposition of the dried nitrate, and the subsequent oxidation, the oxide first produced forms a protecting crust, as it were. This prevents, or at least very materially retards, the decomposition of the material within the interior, *even when the temperature is maintained for several hours at red heat.* On the outside, the material had the appearance of being completely converted to oxide. On powdering the lumps, however, and again heating, there was *in every case* a further evolution of nitric fumes. Moreover, nitrogen itself is often retained by oxides prepared in this way.* It seems thus extremely probable that the quantities of nitrogen measured by Aloy were in every case too small. Obviously, until this point is definitely settled, Aloy's results must be regarded with more or less suspicion.

It has been pointed out that reduction is usually much more complete than oxidation.† During the reduction of an oxide, there is formed, perhaps, by the removal of a portion of the oxygen, a kind of skeleton framework, giving to the remaining substance a porous structure which enables the reducing gas to penetrate farther into the interior of the mass, until reduction is complete. Owing to this action, it is probable that when the green oxide of uranium is finally reduced by hydrogen, all the nitrogen is expelled, and the final product is pure uranous oxide. Consequently, the weight of uranous oxide used in the calculation is probably nearly correct, the principal error being in the volume of nitrogen.

Aside from this special objection to the use of this method in its application to uranium, there is the general objection to the use of such a method where great accuracy is desired. The exact measurement of small quantities of gas offers considerable opportunity for error, especially, when, as in this case, the gas is first to be transferred from the collecting to the measuring apparatus. When the volume or weight of a gas is involved in an atomic weight investigation, it is customary to work with as large volumes as possible, thus reducing to a minimum the effect of the errors inevitably connected with the measurement of the gas. The exact measurement of a volume no larger than 165 cubic centimeters, even, — the largest volume measured by Aloy, — is a matter of considerable experimental difficulty, while with the smaller volumes, 15, 33, and 38 cubic centimeters, errors of at least 0.1% are

* Richards and Rogers, These Proceedings, **28**, 200 (1893); also Richards, Ibid. **33**, 399 (1898).

† Richards and Baxter, loc. cit.

not only possible, but extremely probable. A difference of one tenth of one per cent in the volume of nitrogen makes a difference of 0.3 in the value of the atomic weight. The errors of collection and transference of the gas are more likely to result in reading too small rather than too large volumes, giving too high values for the atomic weight.

From these considerations, it is evident that Aloy's results are at least somewhat doubtful. Aloy gives notice of his intention to apply this method to the determination of other atomic weights, but it is to be hoped that before doing so he will clear up some of the doubtful points in connection with the process. As carried out in this investigation, the method certainly is not a valuable addition to the methods of atomic weight determination.

From the earlier results Clarke computed the value 239.6, while the German Committee recommend 239.5. Both figures are practically identical with Zimmermann's figures.

The investigation herein described was undertaken with the hope that by increasing the experimental basis of our knowledge of the subject, we might be able to reduce to somewhat narrower limits our present uncertainty in regard to the real value of this constant.

Preliminary Work upon the Preparation, Properties, and Methods of Analysis of Some Uranium Compounds.

In view of the well known advantages of the halogen compounds for accurate analysis, when these compounds can be prepared and weighed in a state of purity, — it seemed desirable to use a halogen compound as the basis of a determination of the atomic weight of uranium.

Of the four chlorides of uranium known to exist, none can be prepared in a state of purity that is beyond question. Green uranous chloride, UCl_4, which results from passing dry chlorine over a mixture of uranium oxide and carbon at red heat, is easily converted to the pentachloride, UCl_5, by further action of chlorine at high temperatures. There can be no positive evidence that the green chloride would not contain some of the pentachloride, and if the attempt is made to prepare the pentachloride from the green chloride, it is equally difficult to be sure that the conversion is complete. The trichloride, UCl_3, is made by reducing the tetrachloride with hydrogen, and here again it is difficult to be sure that the tetrachloride is completely reduced. Uranyl chloride, UO_2Cl_2, cannot be prepared in the dry state.

It is extremely probable, then, that any of the chlorides will contain larger or smaller quantities of a higher or lower chloride. It may be

observed, in this connection, that Zimmermann used the chlorides in his vapor density determinations, and his analyses show good agreement. This does not show conclusively, however, that his material was free from small, but fairly constant quantities of higher or lower chlorides as impurities.

On the other hand, bromine forms with uranium only three distinct compounds: the tribromide, UBr_3; uranous bromide, UBr_4; and the oxybromide, or *uranyl* compound, UO_2Br_2. The tribromide can be produced only from the tetrabromide by the action of reducing agents. Uranyl bromide, UO_2Br_2, has been certainly formed only in solution, resulting in hydrated crystals. It has never been definitely obtained in anhydrous form. Zimmermann made many attempts to form the pentabromide, corresponding to the pentachloride, by passing bromine at high temperatures over sublimed uranous bromide. Every attempt gave negative results, showing that at temperatures up to the subliming point of uranous bromide higher bromides cannot exist. Since higher bromides are non-existant under the conditions prevailing in the formation of the tetrabromide, the objections to the use of the tetrachloride are not applicable in the case of uranous bromide. The investigations of Zimmermann* have shown that the tetrabromide can be formed in an apparently definite state. It seemed probable, therefore, from the literature on the subject, that in uranous bromide we had a compound well suited to the purposes of our investigation.

The method of preparation followed at first was essentially that described by Zimmermann.* In an apparatus constructed wholly of glass, a mixture of dry nitrogen and bromine vapor was passed over a mixture of the green oxide of uranium, U_3O_8, and pure carbon. The air was first thoroughly swept out of the apparatus by a current of nitrogen, and the oxide was heated to a high temperature. When the bromine vapor was passed in, uranous bromide formed, and sublimed in brilliant crystalline plates of a brownish color. After cooling in a current of nitrogen, the sublimate was transferred to a weighing bottle. At this point, however, unexpected difficulties arose, owing to the rapid oxidation of the bromide. Uranous bromide is extremely deliquescent, and forms with water and oxygen the oxybromide, with liberation of hydrobromic acid. Consequently, when exposed to the moist air of the laboratory even for the short time required for removing the sublimate from the combustion tube, the bromide loses its brilliant lustre, and

* Annalen der Chemie, **216**, 3.

assumes a dull, greenish yellow appearance, due to formation of the oxy-salt. If not protected from further action of moist air, the salt liquifies completely in a surprisingly short space of time.

In an attempt to change the coating of oxybromide back to the normal salt, recourse was had to the method which has been used successfully in many atomic weight investigations carried on in this laboratory. The salt was transferred to a platinum boat and placed, with a weighing bottle of suitable size, in a glass bottling apparatus.* A stream of dry hydrobromic acid gas was then passed over the bromide at a temperature just below the subliming point of the salt. This treatment, however, fails to restore the original brilliant appearance of the freshly sublimed bromide. The yellow color of the oxybromide still remains. Apparently the oxybromide, once formed, cannot, by this method, be reduced to the normal uranous bromide.

In the previous investigations upon zinc, magnesium, nickel, and cobalt, in which this method of converting oxy-salts to the normal compounds has been used, the presence of even minute quantities of oxy-salt was made known by the opalescence of the solutions on account of the insolubility of these salts. With uranium, however, this method of detecting the presence of uranyl bromide cannot be used, for the oxybromide of uranium is even more soluble than uranous bromide.

The analysis of uranous bromide presents further difficulties. All uranous salts reduce silver nitrate. When a solution of silver nitrate, slightly in excess of the calculated amount, is added to a solution of uranous bromide, the silver bromide first precipitated is probably mixed with metallic silver; for if the silver bromide is filtered off, and the filtrate set aside, finely divided metallic silver soon separates. If a large excess of silver nitrate is added to the uranous bromide, a brilliant purple precipitate is obtained. It is possible that the precipitate may be a mixture of finely divided metallic silver and argentic bromide, or perhaps of normal argentic bromide and the long sought sub-bromide. Although this is an interesting phenomenon, it was not considered advisable to interrupt the research at this period for the length of time necessary for an investigation. The addition of nitric acid prevents the formation of this colored precipitate, but owing to the danger of the loss of bromine, this is not an advisable expedient. Of course it is possible to determine the bromine by first precipitating the uranium and adding silver nitrate to the filtrate, but this introduces

* For a description of this apparatus, see These Proceedings, **32**, 59.

a complexity of operations incompatible with the degree of accuracy requisite in an atomic weight investigation.

On account of these formidable difficulties in the preparation and analysis of pure uranous bromide, it was thought best to search for some compound which offered fewer obstacles. It will be seen that this search was vain, although it required many months.

In view of the great tendency of uranous bromide to oxidize, under ordinary conditions, the use of uranyl bromide seemed to offer the simplest solution of the problem. Anhydrous uranyl bromide has never been prepared in a pure state. In the preparation of uranous bromide, if the nitrogen used contains a little oxygen, or if traces of moisture are present, there is formed, in addition to the uranous bromide, a yellow powder, very different in appearance from the brown color of finely divided uranous bromide. This powder has been assumed by various investigators to be the oxybromide. Owing to the fact that it is always mixed with uranous bromide, an analysis has never been obtained.

There seemed to be, however, some basis for belief that under suitable conditions of temperature, moisture, and oxygen supply, it might be possible to obtain anhydrous uranyl bromide entirely free from the uranous compound. With this end in view, the green oxide, without any admixture of carbon, was heated in a stream of bromine, also in a current of hydrobromic acid. In each case there was apparently no action whatever other than a partial and gradual reduction to the black oxide. This slight reducing action is probably not due to the gases used, in the sense of being peculiar to them, for Zimmermann has shown that this reduction takes place whenever the green oxide is heated in a current of inactive gas such as nitrogen or carbon dioxide. *

Both moist and dry gases were used. Mixtures of these gases and air were also tried, at different temperatures. The green oxide was then reduced by hydrogen to uranous oxide, UO_2, and this was then treated with various combinations of dry and moist bromine vapor, hydrobromic acid, and air, at various temperatures. Again the results were negative. Under these conditions the bromine did not combine to the slightest extent with the uranium. Since combination fails to take place, even in the presence of considerable quantities of oxygen, there is naturally some cause to doubt that the light colored powder above mentioned is really an oxybromide. Possibly it is, after all, uranous bromide in a different state of aggregation.

* Loc. cit. See also Richards, These Proceedings, **33**, 423 (1898).

The hydrated uranyl bromide is more easily obtained. The green oxide was reduced by hydrogen to uranous oxide, suspended in water, and heated with bromine on the steam bath. After driving off the excess of bromine, uranyl bromide remains in solution. The solution may be evaporated to the consistency of a thick syrup, and even under the best conditions the yield of crystals is very small. Moreover, it is almost impossible to wash the crystals free from the mother liquor, since they are extremely soluble in water and alcohol, and ether decomposes the compound, setting free bromine. Hence uranyl bromide was abandoned.

Of the iodine compounds of uranium, the iodate alone seemed promising. This compound has been prepared and described by A. Ditte,* who assigns to it the anhydrous formula $UO_2(IO_3)_2$. The iodate was prepared by us as follows: —

To a solution of uranyl nitrate, containing much nitric acid, was added a solution of iodic acid, prepared by warming finely powdered iodine with nitric acid of specific gravity 1.50. Both solutions were heated to boiling before mixing. Uranyl iodate is precipitated as a yellow, finely crystalline salt, but slightly soluble in water at ordinary temperatures. At 100°, however, if some nitric acid is added, it is possible to obtain a solution containing ten grams of iodate to the litre. On cooling, 2.5 to 3.0 grams of iodate crystallize out. By recrystallizing a few times, in sufficiently large vessels, it is possible to obtain a compound in a high state of purity.

The method of preparation described above is that recommended by Ditte. Although Ditte's course of procedure was carried out as exactly as possible, the compound obtained differed from that which he describes. Instead of being anhydrous, it contained one molecule of water. Inasmuch as Ditte's statement of the amount of nitric acid which he used is extremely vague, different concentrations were tried, from a solution slightly acid up to one containing twenty-five per cent of strong nitric acid. In every case the hydrated compound was obtained. Ditte did not recrystallize his compound, but our recrystallized product was identical with that which was only once precipitated. The analysis given is the average of ten concordant analyses of material prepared from both hot and cold solutions. Both recrystallized iodate and that precipitated only once are represented. The method of analysis is described below.

* Annales de Chimie et de Physique, 6th Series, **21**, 158 (1890).

ANALYSIS OF URANYL IODATE.

	Found.	Calculated for $UO_2(IO_3)_2H_2O$.
Uranous oxide	42.54%	42.34%
Iodic acid	54.84	54.84
Water (by difference)	2.62	2.82
	100.00%	100.00%

In determining the composition of the iodate, a weighed quantity of the substance was used, and the percentage composition by weight calculated in the usual manner. For an atomic weight determination, however, any method which involves the original weight of a salt crystallized from solution as a factor in the calculation must of course be avoided on account of the ever present possibility of included mother liquor. It was necessary, then, to determine directly the ratio of iodine to uranium, or to uranium oxide. To determine the uranium, advantage was taken of the behavior of the iodate on ignition. When heated, the iodate is decomposed, water, oxygen, and iodine being given off, leaving uranium oxide. The process was carried on in an ordinary combustion tube of hard glass, a current of dry air being passed through the tube. Since Zimmermann has shown that the green oxide undergoes partial reduction at high temperature unless in an atmosphere of oxygen, * a stream of oxygen was finally passed through the tube. The oxide was then cooled in an atmosphere of oxygen. Treated in this way, the decomposition of the iodate is not complete. Some iodine always remained in the oxide, even when the heat was maintained for three hours at a temperature just below the softening point of the combustion tube. To correct for this amount of iodine, the oxide was weighed, dissolved in dilute nitric acid, and the iodine precipitated as argentic iodide. The amount of iodine found in this way varied from 0.1% to 1.0% of the total iodine, according to the duration of the period of ignition.

Iodine was determined in another sample of material exactly similar to that used for the uranium. The method was, briefly, reduction of the iodate by sulphurous acid, and precipitation with silver nitrate. Stas has shown that silver iodate can be converted completely and without loss into silver iodide by the use of sulphurous acid, † and the same

* Annalen der Chemie u. Pharmacie, **232**, 287 (1886).

† Untersuchungen über die Gesetze der chemischen Proportionen über die Atomgewichte u. ihre gegenseitigen Verhältnisse, J. S. Stas. Aronstein's translation, p. 69.

method applies equally well to uranium iodate. The iodate was suspended in 200 c.c. of water acidified with 20 c.c. sulphuric acid, cooled in ice to 0°, and pure sulphur dioxide was passed in until the solution smelled strongly of this reagent. The flask was then removed from the ice and shaken occasionally. From three to four hours is required before complete reduction takes place and the last traces of iodate go into solution. When completely reduced, silver nitrate is added, and heated to 60° in order to cause the more coherent deposition of the precipitate.* Thus it was found possible to convert the insoluble iodate into soluble iodide without loss of iodine.

In this way the ratio of uranium oxide to iodine may be determined, regardless of the presence of occluded water in the iodate used, provided that the amount of water occluded be exactly the same in each of the samples. It would obviously be more satisfactory to determine both uranium and iodine in the same sample, provided a sufficiently simple method could be found.

The following method was found to fulfil the required conditions fairly well. A quantity of the iodate was placed in a boat in a combustion tube, to one end of which was attached, by a ground glass joint, a weighed U-shaped tube. The free end of this tube was drawn out and fused to a smaller tube which dipped into a solution of sulphurous acid. On heating the iodate in a stream of air and oxygen, the salt was decomposed and the iodine was carried over and condensed in the U-tube, which was packed in ice. The small quantity of iodine vapor not condensed was collected in the sulphurous acid and precipitated as silver iodide. The heating was continued for an hour after no more iodine could be seen coming off. The end of the U-tube was then sealed by fusing off the small tube, and the other end was closed by a ground glass stopper immediately after disconnecting from the combustion tube. In this way about ninety-nine per cent of the total iodine was weighed directly as free iodine. Of course the small amount of iodine remaining in the oxide after ignition had to be determined separately, as already described. By this method the amount of iodine found was practically identical with that found by the sulphurous acid method.

In determining the iodine present in the oxide after ignition, it has been assumed that the iodine is present as iodide. Although it is hard

* When silver iodide is precipitated in the presence of sulphurous acid, the supernatant liquid does not become clear enough to filter even after several days, unless heated to 60°.

Vide Stas, "Untersuchungen," p. 69.

to believe that at the temperature employed any of the iodine can exist as iodic acid, it is impossible to prove the point experimentally. The uncertainty in regard to this point renders the use of the method inadvisable where the greatest possible accuracy is desired. Hence none of these analyses have any significance as a basis for computing the atomic weight of uranium.

Besides the bright yellow, slightly soluble iodate, we prepared a paler yellow, more soluble, and more highly hydrated salt, which suffers transition quickly into the earlier compound at a high temperature and more slowly at a low temperature. Double iodates with sodium and potassium were also prepared. Some of our observations were inconsistent with the published record concerning the subject; but in spite of our desire to clear up the uncertainty and to study the rather interesting transition phenomena, we abandoned the iodates because none of them gave promise of a precise basis for the determination of the desired atomic weight.

The next compound investigated was the oxalate, which has the composition $UO_2C_2O_4 \cdot 3H_2O$. Owing to the comparatively slight solubility of this compound it can be obtained in a state of great purity by a few crystallizations.

The best method of analysis is that of dry combustion, the carbon dioxide being absorbed in potash in the usual manner. The uranium is left in the combustion tube as the green oxide, U_3O_8, and consequently can be compared directly with the weight of carbon dioxide obtained. This obviates the necessity of using the weight of the oxalate as a factor in the calculation of the atomic weight, and so eliminates the error due to included water. As already mentioned, this method has been used by Ebelmen and Péligot in their determination of the atomic weight of uranium. There is in this method a possible source of error, difficult of detection and correction, but none the less dangerous, in the possibility that the uranium oxide may after combustion still retain traces of carbon. Moreover, it became evident, after a few analyses had been made, that combustion analysis, as ordinarily conducted, is an exceedingly questionable method where great accuracy is desired. The great difficulty in obtaining absolute "blanks" is well known. Our experience amply confirmed the observations of Mabery,* Auchy,† and others in regard to

* Inaccuracies in the Determinations of Carbon and Hydrogen of Combustion, C. F. Mabery, Journal Am. Chem. Soc., **20**, 510 (1898).

† George Auchy, Journal Am. Chem. Society, **20**, 243 (1898).

the loss of water and possibly of carbon dioxide from the ordinary form of potash bulbs. We also found a single sulphuric acid tube entirely insufficient to absorb all the water. Clearly, then, if we were to use this method, an elaborate investigation of the form of apparatus, method of procedure, and limits of error, was absolutely imperative. The use of the oxalate, however, did not seem sufficiently promising to warrant the necessary expenditure of time.

After thus investigating the uranium compounds which seemed likely to furnish a suitable basis for an atomic weight determination, anhydrous uranous bromide, in spite of its disadvantages, seemed most likely to fulfil the necessary requirements. As already mentioned, this compound oxidizes with the greatest ease on exposure to moist air. It was necessary, therefore, to devise apparatus which should preclude any possibility of bringing the sublimed bromide in contact with the air of the laboratory until it had been collected and weighed. After much experimenting with different forms of apparatus, the following method was adopted.

Preparation and Collection of Pure Uranous Bromide.

The mixture of urano-uranic oxide and carbon was placed in a porcelain boat within the larger of two "telescoping" porcelain tubes. The portion of the tube containing the oxide was heated in a Fletcher furnace, and after thoroughly sweeping out the apparatus with dry nitrogen, a mixture of dry nitrogen and bromine vapor passed over the oxide. The sublimed bromide collected near the inner end of the smaller porcelain tube. The very efficient and elaborate desiccating apparatus which served so well in the work on the atomic weights of cobalt and nickel, was very kindly given by Dr. Baxter for use in this investigation.* This apparatus, with slight modifications, was used for drying the nitrogen and bromide, and was connected by a ground glass joint with the porcelain combustion tube.

With this apparatus traces of air diffused through the annular joint between the porcelain tubes, forming a coating of oxide on the inner tube.† In the case of uranium, the oxide is found to be copiously mixed with the sublimate also. This diffusion of air takes place even when the outer end of the inner porcelain tube is nearly closed, thus making a considerable outward current within the tubes.

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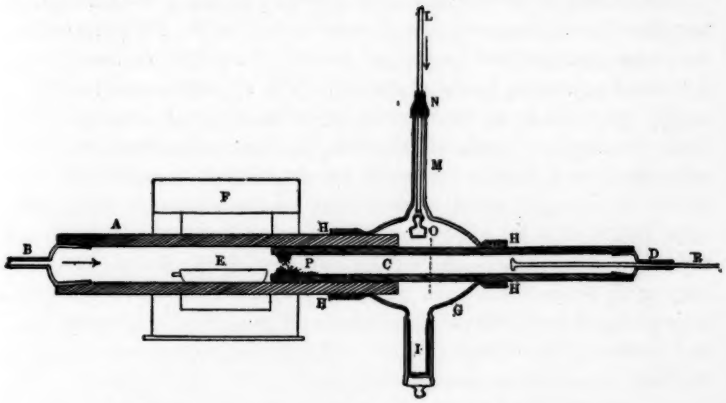
* For a full description of this apparatus see There Proceedings, **33**, 124 (1897).

† In the case of cobalt and nickel this oxide was easily removed by subsequent treatment, but in the present case removal was impossible.

In order to obviate the difficulty and exclude air a glass jacket was slipped over the joint between the tubes. The construction and use of this jacket will be made clear by reference to the accompanying drawing.



SECTION OF SUBLIMING AND BOTTLING APPARATUS.

A, outer porcelain tube fitted with ground-glass joint B; C, inner porcelain tube with ground-glass stopper D; E, boat containing oxide and carbon; F, furnace; G, glass jacket; H, H, H, H, packing of asbestos wool; I, weighing bottle; L, tube for admitting nitrogen, sliding within tube M through rubber connection N, and carrying at its end stopper O of weighing bottle; P, sublimate; R, rod for removing sublimate.

The jacket was drawn down at the ends, so as to fit the porcelain tubes A and C as well as possible, and the spaces between the tubes and the jacket were packed tightly with asbestos wool. This packing makes a joint sufficiently tight to withstand a pressure equal to that of eight or ten centimeters of water. The jacket was provided with a long tube, M, within which slid a second tube, L, connection being made by means of the short piece of rubber tubing, N. To the end of the inner tube was attached, by platinum wires, the stopper, O, of the weighing bottle. The outside diameter of L was very little less than the inside diameter of M, thus leaving very little space between the walls of the two tubes. For this reason, and also on account of the length of the tube M, — about fifteen centimeters, — there was little danger of bromine diffusing up in sufficient quantities to attack the rubber connection, N. Even if this were the case there could be no possibility of contamination of the sub-

limate thereby, since there was always a constant outward pressure of bromine during the sublimation. The outer end of L was connected with the nitrogen supply of the desiccating apparatus. All glass joints and stop-cocks were lubricated with syrupy phosphoric acid.

The method of procedure was as follows: In the porcelain boat, E, was placed an intimate mixture of urano-uranic oxide and pure carbon, the carbon being about twenty per cent of the weight of the mixture, thus insuring a large excess of carbon. The apparatus was then thoroughly swept out by nitrogen, which enters at B and L simultaneously. After the air was completely expelled, the combustion tube was gradually raised to a high temperature by the blast lamp. Heating in a current of nitrogen was then continued for three hours at least, sometimes longer, in order to insure complete removal of all traces of air and moisture. During this and subsequent operations, the outlet of the stopper D of the inner tube was nearly closed by asbestos wool, thus maintaining a constant and considerable pressure within the apparatus, and hindering the diffusion of air. After this preliminary heating in nitrogen, bromine vapor was passed in through B. During the first trials of the apparatus it was our practice to keep a slow current of nitrogen passing in at L during the sublimation. This kept the jacket entirely free of bromine, a very slow current of nitrogen being sufficient to keep any bromine from passing between the walls of the porcelain tubes. It was found, however, that traces of air diffused through the permeable asbestos packing, and were of course carried into the combustion tube by the current of nitrogen, forming on the inner tube a coating of oxide, and contaminating the sublimate. In order to avoid this, the nitrogen was shut off from L sometime before turning on the bromine. After turning on the bromine, the jacket slowly filled with dilute bromine vapor. While the greater part of the sublimate collected within the inner tube, a little collected between the walls of the two tubes, almost sealing the annular space. This sublimate, which collected on the outside of the inner tube, is a valuable indicator of the condition of the sublimate within. In the presence of mere traces of oxygen the lustrous brown color of the uranous bromide gives place to a dull yellow color easily distinguishable. Comparatively small quantities of oxygen form a coating of black oxide. When the sublimation is conducted according to the method described, the outside of the inner tube is free from any traces of the supposed oxybromide or of oxide, thus showing that no appreciable quantity of moist air could have reached the innermost portions of the sublimate. The best proof of the purity of the sublimate is of course

found in the agreement of analyses of substance formed under various conditions of bromine supply.

After the bromine had been run for about one and a half hours, the sublimate was cooled for three hours in a current of nitrogen. When the tubes were thoroughly cold, nitrogen was finally passed into the jacket through L, in order to sweep out any traces of bromine that might still remain. The inner tube, containing the sublimate, was then carefully drawn out until the inner end reached a position over the mouth of the weighing bottle, indicated in the diagram by the dotted line. This can be done without seriously disturbing the asbestos packing, a rapid current of perfectly dry nitrogen being admitted meanwhile through L. By means of the glass rod, R, the sublimate was pushed out of the tube and dropped into the weighing bottle, I. The tube L, carrying the stopper, was then pushed down and the stopper inserted. The stopper was held by the platinum wires so lightly that after pushing it into place the tube L could be withdrawn, leaving the stopper inserted in the bottle.

Thus uranous bromide was sublimed, collected, and bottled up in an atmosphere of dry nitrogen ready for weighing, without once coming in contact with the air of the laboratory. That the apparatus is effective for the purpose intended, and capable of producing material of constant composition, was shown by the first rough analyses of uranous bromide, which yielded 57.41, 57.41, and 57.42 per cent bromine respectively. These analyses were made with material that had not been purified, but served to show the constancy of composition of the sublimate; for not only was the length of time occupied in the sublimation varied, but in one case the sublimate was cooled in bromine instead of in nitrogen. Of course if an appreciable amount of an oxygen compound were formed, by diffusion of air or moisture, there would almost certainly be discrepancies in the results, since it is hardly conceivable that under the varying conditions exactly the same quantities of oxy-salt should be formed each time.

Because the specific gravity of uranous bromide was unknown, the following determinations were made: 2.0328 grams of the salt displaced on one occasion 0.3332 gram of kerosene at 21°, and at another trial 0.3322 gram. The kerosene had been redistilled, and only the high boiling portion was used. The density of the kerosene at 21°, referred to water at 4°, was 0.7919. Hence the specific gravity of the uranous bromide was (1) 4.830 and (2) 4.846, giving as the mean 4.838. This value was used in reducing the observed weights of bromide to the vacuum standard.

During the weighing in the final analyses, the bromide of uranium was still surrounded by an atmosphere of pure dry nitrogen in the tightly stoppered weighing bottle. Since this bottle had been full of dry air when it was first weighed, a small correction had to be applied on this account. The difference in weight between 6.70 cubic centimeters (the interior volume of the weighing bottle) of air and the same volume of nitrogen at 20° C. is 0.000265 gram. Of this nitrogen a gram of uranous bromide displaced $\frac{1}{4.84} = 0.206$ cubic centimeters, or 0.24 milligram, while the brass weights used in weighing the bromide displaced 0.145 milligram of air. Hence in vacuum a gram of uranous bromide would weigh $0.265 + 0.24 - 0.145 = 0.36$ milligram more than the observed weight, while two grams would weigh $0.265 + 2(0.24 - 0.145) = 0.46$ more than the observed weight. All the weights given in the tables are corrected in this way to the vacuum standard.

Methods of Analysis.

By the use of these devices we were able to prepare and weigh pure uranous bromide in a definite state. There still remained, however, the problem of devising a suitable method of analysis. As previously mentioned, all uranous compounds reduce silver nitrate, making impossible the usual method of procedure in halogen determinations.

The method of precipitating the uranium and determining bromine in the filtrate involves too much danger of loss of material in the multiplicity of operations. The most satisfactory solution of the problem seemed to be to oxidize the compound to the uranyl salt, provided this could be done without loss of bromine. Nitric acid is of course effective as an oxidizing agent, but the oxidation is accompanied by loss of bromine. After much experimenting, hydrogen dioxide was found to be the most suitable oxidizer. From neutral solutions of uranium compounds, hydrogen dioxide precipitates a hydrated peroxide of uranium. If the solution is slightly acid, this precipitation is prevented and the uranous compound completely oxidized to the uranyl state. The weighed sample of uranous bromide was dissolved in considerable water — at least 400 cubic centimeters of water to each gram of bromide. The bottle containing the bromide was opened by means of a suitable glass fork, either below the water or just above the surface, so that it could be instantly submerged, and thus avoid loss of hydrobromic acid by the action of moist air. The calculated volume of a standard solution of pure hydrogen dioxide was then diluted to about 100 c.c., one cubic centimeter of pure dilute sul-

phuric acid was added, and the mixture was slowly run into the solution of uranous bromide. The green color of the uranous salt soon changes to the yellow color characteristic of uranyl compounds. On adding the first few cubic centimeters of the dilute hydrogen dioxide solution, a greenish white precipitate came down. Addition of more of the acid dioxide solution redissolved it, and the resulting solution was perfectly clear. This peculiar hydrolytic action is due to the acid, and not to the hydric dioxide, for the same reaction occurs if dilute sulphuric acid alone is added to the solution.

The explanation of this interesting phenomenon, which is just the opposite of what might have been expected, is, undoubtedly, that the bromide is already hydrolyzed to a great extent by merely dissolving in water. The hydrate is probably in solution in the colloidal state. Evidence of this is found in the fact that if the clear aqueous solution of uranous bromide is allowed to stand exposed to the air, a hydrate gradually separates, giving to the solution a cloudy, murky appearance. After two or three days this precipitate disappears, giving place to a clear yellow solution of oxybromide and hydrobromic acid. The addition of sulphuric acid coagulates the colloid before it can all be converted into uranyl salt.

In order to be sure that no bromine or hydrobromic acid is lost by this method of oxidation, the following experiment was made. 0.5 gram of bromide was dissolved in 250 c.c. of water, 50 c.c. of dilute sulphuric acid (1 : 10) was added, and the hydrogen dioxide solution was run in. This was done in a closed flask, similar in construction to a gas washing bottle. A current of air was drawn through the bottle and then through starch solution containing potassium iodide to see if bromine is liberated. Not the slightest trace of blue color appeared in the starch solution, even after adding a large excess of hydrogen peroxide and allowing it to stand over night. A test for hydrobromic acid was sought in a similar way, by drawing the air through a solution of silver nitrate, again with negative results, as was to have been expected. These experiments show conclusively that uranous bromide can be oxidized completely by hydrogen dioxide, without loss of bromine.

Silver nitrate, in moderately concentrated solutions, is not acted upon by a three per cent solution of hydrogen peroxide. Consequently a considerable excess of the latter reagent could do no harm. Nevertheless care was taken never to add more than the calculated amount of hydrogen dioxide. Moreover, the solution of hydrogen dioxide used contained only one per cent of this reagent, and this was diluted ten times before

adding to the bromide solution, thus reducing to a minimum the possibility of too vigorous oxidation, with consequent liberation of bromine.

After the oxidation, bromine was precipitated by pure silver nitrate in the usual manner. This precipitation was conducted in an Erlenmeyer flask fitted with a ground glass stopper. The silver bromide was collected on a Gooch crucible, and dried in an electrically heated drying oven. Of course the asbestos shreds carried away in washing the silver bromide were collected by passing the filtrate and wash water through a fine filter, and their weight was added to that of the silver bromide. The bromine determination was carried on in orange colored light.

It was found in the work upon cobalt and nickel that the porcelain tube is attacked by bromine vapor at the high temperature employed during the sublimation, with the result that sodium bromide was always present in the sublimate. In these investigations this impurity was determined by the reduction of the bromide to the spongy metallic state by means of hydrogen, and extraction by water.* A somewhat similar method was tried with uranium. Since hydrogen reduces uranous bromide only to the tri-bromide, the bromide was ignited in a current of air and the resulting oxide leached with water. It was found to be impossible to oxidize the bromide completely. A little uranous bromide invariably remained and was washed out with the alkali. Both dry and moist air was tried, also ignition in steam, but in every case uranium was washed out in considerable quantity.

Precipitation of the uranium by hydrogen dioxide was next tried, but it was found impossible to precipitate the uranium completely. The rather unsatisfactory method of determining the sodium in the filtrate from the bromine precipitation, or in a new sample of uranous bromide as nearly similar as possible, after removing the uranium with ammonium sulphide, appeared to be the only available method. The filtrate and wash waters from the bromine precipitation were evaporated in platinum to small bulk, and the uranium and excess of silver precipitated by pure colorless ammonium sulphide. This reagent precipitates uranium completely. The filtrate was then evaporated to dryness, the ammonium salts expelled by ignition, and the residual sodic nitrate converted to the sulphate and weighed as such. Of course these operations were all conducted in platinum vessels. This method of work is not wholly satisfactory, on account of the complexity of operations involved, but it seems to be the only practical method.

* These Proceedings, **34**, 329, 359 (1899).

Purification of Materials.

As the source of uranium, commercial "chemically pure" uranium acetate was used.* This was first converted to the chloride on account of the greater solubility of this compound, — by precipitation as ammonium uranate and redissolving in dilute hydrochloric acid. To the hot and slightly acid solution, pure sulphuretted hydrogen was added to saturation. The free acid was then neutralized with ammonic hydroxide, a slight excess of the alkali was added, and more sulphuretted hydrogen was run in. In this way some uranyl sulphide was precipitated, in order to sweep down with it any colloidal sulphides of the higher groups which might otherwise escape removal. The excess of sulphuretted hydrogen was boiled off, and after standing over night the supernatant liquid was decanted through a washed filter.

The next step depended upon the fact that uranium remains in a solution of the double carbonate of ammonium and uranium, in the presence of an excess of ammonium sulphide, while all the other members of the aluminum and iron groups are thrown down by this reagent. Consequently ammonic hydrate and ammonium carbonate in slight excess were added to the filtrate, forming the double carbonate. If the solutions are concentrated, the double carbonate is precipitated when more than a slight excess of ammonic carbonate is used. This happened in some cases, when it was necessary to redissolve the precipitate in dilute hydrochloric acid and again add ammonic carbonate in more dilute solution. About fifty grams of carbonate per litre was found to give the best results. Ammonic hydroxide was then added to the hot solution, and sulphuretted hydrogen in excess. After standing over night the solution was filtered. In several of the more concentrated solutions, a considerable quantity of the salt crystallized out. These crystals were worked up separately, as they were probably purer than the solution. On boiling the solution to decompose the excess of ammonium sulphide, some of the ammonic carbonate was decomposed, causing the precipitation of some uranium sulphide. This precipitate was discarded, as it might have contained iron, or other analogous metals which had previously escaped precipitation. Dilute hydrochloric acid in slight excess was added, and the carbon dioxide was expelled by boiling. The free acid was then almost neutralized with pure ammonic hydroxide, and

* This method of uranium purification, with some modifications and additions, is similar to that employed by Zimmermann. Annalen der Chemie u. Pharmacie, **232**, 299.

pure ammonic sulphhydrate added in excess. The color of the resulting precipitate of uranium sulphide varies greatly with the temperature. In warm solution it was at first reddish brown, while that precipitated in the cold varied from bright red to brownish yellow. On washing, all turn black, the sulphide being decomposed into uranous oxide and sulphur. After thorough washing the resulting mixture of oxide and sulphur was ignited in a porcelain dish, the green urano-uranic oxide being the product.

The oxide was then dissolved in a platinum dish in redistilled nitric acid, evaporated, and recrystallized from nitric acid solution. Uranyl nitrate does not crystallize well from aqueous solution, but it was found that if a little nitric acid is added, it crystallizes readily in fairly large monoclinic prisms. This recrystallization was repeated ten times from acid solution, and finally twice from aqueous solution. Finally the pure nitrate was converted to the oxide by ignition in platinum. A second sample, used in the preliminary series, was prepared by repeated fractionation of the mother liquors of the first sample.

Since this work was carried out, Sir William Crookes * has published the account of several methods by which he was able to prepare specimens of uranyl nitrate which were not radio-active. The radio-activity of uranium has hitherto been supposed to be characteristic of this element. Crookes has shown, however, that this is not the case, but that the active element can be separated by treatment with ether, by fractional crystallization, or by treatment with excess of ammonium carbonate. Unfortunately none of the pure oxide prepared for this investigation remained, hence it is impossible to test directly its radio-activity. Since two of Crookes's methods were used in purifying our material, viz. the ammonium carbonate treatment and fractional crystallization, it is highly improbable that our oxide was radio-active. In repeating Crookes's work with nitrate made from some of the same material used in preparing our best nitrate, it was found that a sample of the *fifth* crystallization gave no trace of action on twenty-four hours exposure to a quick photographic plate. The material used in this experiment had not been submitted to the ammonium carbonate treatment. When it is considered that the material used for our atomic weight determinations was first put through the carbonate process, — in itself sufficient to remove the radio-active element, — and then was recrystallized *twelve times* as nitrate, it would seem that our pure oxide must have been free from all radio-active material.

* Proceed. Lond. Royal Soc., **66**, 409 (1900).

There is another phase of this subject that deserves to be considered, namely, the possible effect of radio-active matter, even if present, upon the atomic weight value. The purest specimen of radium or "polonium" yet obtained has consisted of a mixture containing probably little more than fifty per cent of the active element, as nearly as could be estimated. This highly impure material, however, possesses 8,000 times the radio-activity of uranium. The radio-active power of the pure material is undoubtedly very much greater than that of the impure mixture. Consequently the quantity of ratio-active substance necessary to give to uranium the comparatively slight degree of activity that it possesses must be exceedingly minute. Giesel has recently shown * that a quantity of radium so small that it cannot be detected by sulphuric acid is sufficient to affect a photographic plate. Crookes also says on this point, "Considering my most active UrX does not contain sufficient of the real material to show in the spectrograph, yet is powerful enough to give a good impression on a photographic plate in five minutes, what must be its dilution in compounds which require an hour, a day, or a week to give an action?" † Even in the ordinary active uranium compounds it is most unlikely that the active element — if indeed it is an element — could possibly be present in quantity sufficient to exert any influence whatever upon the atomic weight of uranium.

Pure carbon was obtained by ignition of sugar. Large, clear crystals of the best "rock candy" of commerce were ground up in a porcelain mortar and ignited at low heat in a platinum dish as long as organic gases were given off. The resulting charcoal was then powdered in an agate mortar and ignited in a hard glass combustion tube; first in a stream of pure, dry nitrogen, and finally in a stream of bromine vapor. In this way the carbon was freed from any impurities which might, if present, be acted upon during the sublimation and contaminate the sublimate. Owing to the presence of undecomposed carbohydrates, or possibly of water, most of the bromine was converted into hydrobromic acid. Heating in bromine was continued until acid fumes ceased to be given off. Finally, the carbon was again heated in a current of dry nitrogen. Five grams of carbon, thus prepared, left no visible or weighable residue after combustion in oxygen.

The method of bromine purification was essentially identical with that used in many other atomic weight investigations in this laboratory, and has

* Berichte der deutschen chemischen Gesellschaft, **33**, 3569 (1900).

† Proceed. Lond. Royal Soc., **66**, 422 (1900).

been proved by long experience to be the most efficient and satisfactory. Commercial, "pure" bromine was partially freed from chlorine by shaking with a fifteen per cent solution of potassic bromide. One fourth of the bromine was then converted to calcic bromide by running it slowly into milk of lime in the presence of a large excess of ammonia. The calcic bromide solution was filtered and concentrated by evaporation, and the rest of the bromine was added to it. A little zinc oxide was then added, and after standing over night the bromine was distilled, nearly free from chlorine. Most of the iodine is removed as zinc iodate. After redistilling the bromine, in order to remove any calcium bromide that may have spattered over in the first distillation, it was converted into hydrobromic acid by slowly dropping it into a mixture of red phosphorus and hydrobromic acid. The red phosphorus was at first washed free from chlorides. The hydrobromic acid, containing some free bromine, was distilled. The free bromine liberates any iodine which may have escaped the zinc oxide. The first portion of the distillate, containing free bromine and iodine, and organic matter, was rejected, and so was the last portion, which may have contained traces of arsenic. The hydrobromic acid was then converted into bromine by distilling over pure manganese dioxide previously treated with sulphuric acid and washed. One half the bromine is obtained by the manganese dioxide alone. As soon as no more bromine comes off, a little redistilled sulphuric acid is added, and the rest of the bromine was obtained. It was then redistilled several times, rejecting the first and last portions, and finally dried over pure phosphorous pentoxide.

The silver precipitation also presents no new features, except, perhaps, its somewhat unusual thoroughness. Partially purified silver was dissolved in nitric acid, diluted, and precipitated with pure hydrochloric acid. After thorough washing the chloride was reduced by invert sugar and sodic hydrate which had been purified by electrolysis. The metallic silver was thoroughly washed, dissolved in nitric acid, and again precipitated as chloride and reduced. It was then dried and fused on charcoal; the lumps of silver were cleaned with sand, dissolved in pure nitric acid, diluted to a volume of two litres, and again precipitated with pure hydrochloric acid. The resulting chloride was then digested on the steam bath with aqua regia, washed, and once more reduced by invert sugar and sodic hydrate. After drying, it was fused on pure sugar charcoal. The buttons of silver were cleaned with sand, and then purified electrolytically, a small portion being dissolved in nitric acid to serve as the electrolyte, and the rest serving as anode material. The

crystals of electrolytic silver were then dried over potash and fused in vacuo on a boat of pure lime. The buttons of silver thus obtained were treated with nitric acid to remove the surface, dried, and kept over potash. A second sample was obtained by fusing in vacuo electrolytic silver which had been prepared from the silver bromide obtained in Dr. Baxter's work upon cobalt, which was known to be very pure.

Hydric dioxide was purified as follows: To a solution of the ordinary commercial peroxide prepared for medicinal use, was added a solution of baric hydroxide, which had been purified by recrystallization. The precipitated baric dioxide was washed until a nitric acid solution of the same showed no trace of halogen. It was then added to pure dilute sulphuric acid, and the resulting solution of hydric dioxide was filtered and distilled in a partial vacuum. The solution thus obtained showed no trace of halogen, and left no visible residue on evaporation in platinum.

Ammonium sulphide was made from pure ammonia, which had been redistilled in platinum, and pure sulphuretted hydrogen. It left no visible residue on evaporation in platinum.

Hydrochloric and nitric acids were redistilled in a platinum still, and throughout the work platinum vessels were used wherever possible.

Water was twice redistilled, once over alkaline potassic permanganate, and again over acid potassic sulphate from a Jena glass flask, a block-tin condenser and Jena glass receiver being used.

The Results of the Analyses of Uranous Bromide.

The method of analysis has been already fully described.

The analyses recorded in the first series were made by adding an excess of silver nitrate to the solution of uranyl bromide. From the ratio of the observed weights of uranous bromide to argentic bromide, the molecular weight of uranous bromide was calculated, that of argentic bromide being assumed to be 187.885. From the results obtained from this preliminary series the weight of silver necessary to precipitate the bromine in one gram of uranous bromide was calculated. In the subsequent determinations the exact weight of silver required was weighed out, as nearly as possible, and dissolved in pure nitric acid with suitable precautions to avoid loss. The exact end point was reached by standard hundredth normal solutions of argentic nitrate and hydrobromic acid, by means of the nephelometer.* After determining the end point a slight excess of argentic nitrate was always added, and the weight of the total

* Richards, These Proceedings, **30**, 385 (1894). Z. anorg. Chem., **8**, 269 (1895).

argentic bromide determined. Thus from each of these analyses two distinct ratios were obtained as a basis for the calculation of the molecular weight of uranous bromide, — the ratio of uranous bromide to argentic bromide, and that of uranous bromide to silver.

As would naturally be expected from the complexity of operations involved, determinations of the sodium in the filtrates from the argentic bromide gave unsatisfactory results. The large quantity of filtrate and wash waters had to be evaporated to small bulk, the uranium precipitated, and the sodium determined in the residue. It seemed advisable to make a series of separate analyses for sodium only, and use the average percentage of sodium found as a constant correction. This method was used in the work upon cobalt and nickel.*

Accordingly three alkali determinations were made, *wholly in platinum*, the material not coming in contact with glass at any time except during the original collection and weighing of the sublimed bromide. The sublimate was dissolved in pure water, in a platinum dish, and the uranium was precipitated with pure ammonium sulphide. The ammonium sulphide was freshly prepared for each analysis, wholly in platinum. It left no residue on evaporation in platinum. The precipitated sulphide was digested on the water bath to expel most of the excess of ammonium sulphide, filtered through a platinum funnel, and the filtrate and wash water evaporated to small bulk in a platinum dish. The sodium bromide was then converted to sodium sulphate and weighed. The following table contains the data and result: —

No.	Weight of Uranous Bromide.	Weight Sodic Sulphate obtained.	Equivalent Weight of Sodic Bromide.	Per cent Sodic Bromide.
	grams.	gram.	gram.	
1	1.656	0.00092	0.00133	0.081
2	2.629	0.00143	0.00207	0.079
3	1.407	0.00121	0.00175	0.124
			Average	0.095

The average of these three determinations, 0.095, per cent, is practically identical with the amount of sodic bromide found in the cobalt and nickel work, which was 0.10 per cent. The porcelain tubes used in this inves-

* These Proceedings, **34**, 339, 365 (1899).

tigation were of the same manufacture as those used in the nickel and cobalt work, and since the method of preparation of the three bromides was practically the same, probably the quantity of sodium extracted from the tubes by the action of the hot bromine vapor was the same, — *on the average*, — in all three cases, and not far from 0.10 per cent. Consequently, in calculating the following results, this value was used as a constant correction. The effect of applying the correction is to raise the calculated atomic weight about two tenths of a unit. Of course by this method the quantity of sodic bromide calculated will vary somewhat from the exact quantity present, *in individual determinations*. The *average* result, however, will undoubtedly vary but little from the result obtained if the alkali could be determined in each sample. It certainly is very much nearer the truth than the results to be obtained by the cumbersome method of determining the alkali in the filtrate from each precipitation of argentic bromide.

Analysis No. 2 was rejected on account of contamination of the uranous bromide by shreds of asbestos from the packing of the jacket, and No. 4 was not used because the combustion tube cracked during sublimation, rendering probable the formation of some oxybromide. The silver required in analysis No. 6 was determined for practice preparatory to the final series, being 0.9087 gram when all corrections were applied. It is not included in the table, since its nature was essentially preliminary. As usual, all weighings were reduced to the vacuum standard. While all

THE ATOMIC WEIGHT OF URANIUM.

O = 16.000; Ag = 107.93; Br = 79.955.

FIRST SERIES (PRELIMINARY). $UBr_4 : 4AgBr$.

No. of Analysis.	Total Weight of Uranous Bromide + Sodium Bromide in vacuo.	Weight of Uranous Bromide corrected for NaBr.	Total Weight of Silver Bromide in vacuo.	Weight of Silver Bromide corrected for NaBr.	Parts of Uranous Bromide equiv. to 100 parts Argentic Bromide.	Atomic Weight of Uranium.
	grams.	grams.	grams.	grams.	grams.	
1	2.20795	2.2058	2.97391	2.9699	74.272	238.36
3	1.44321	1.4418	1.94272	1.9401	74.316	238.69
5	1.40639	1.4050	1.89355	1.8910	74.299	238.56
6	1.17607	1.1749	1.58396	1.5818	74.276	238.39
				Average	74.289	238.50

SECOND SERIES. $UBr_4 : 4AgBr$.

No. of Analysis.	Weight of Uranous Bromide + Sodic Bromide in vacuo.	Wt. of Uranous Bromide corrected for Sodic Bromide.	Total Weight of Silver Bromide in vacuo.	Weight of Silver Bromide corrected for NaBr.	Parts of Uranous Bromide equiv. to 100 parts Argentic Bromide.	Atomic Weight of Uranium.
	grams.	grams.	grams.	grams.	grams.	
7	1.80174	1.7999	2.42588	2.4226	74.296	238.54
8	1.06723	1.0662	1.43713	1.4352	74.290	238.50
9	1.85698	1.8551	2.50009	2.4967	74.302	238.59
				Average	74.296	238.54

THIRD SERIES. $UBr_4 : 4Ag$.

No. of Analysis.	Weight of Uranous Bromide with all Corrections.	Weight of Silver in vacuo (not corrected for Sodic Bromide).	Weight of Silver with all Corrections.	Wt. of Uranous Bromide corresponding to 100 grams Silver.	Atomic Weight of Uranium.
	grams.	grams.	grams.	grams.	
10 (7)	1.7999	1.39365	1.3918	129.322	238.49
11 (8)	1.0662	0.82559	0.8245	129.315	238.46
12 (9)	1.8551	1.43617	1.4342	129.347	338.60
			Average		238.52

Average of all determinations 238.52
Average of six final determinations 238.53

the weighings were actually made to the hundreths of a milligram the final corrected data are rounded off to the nearest tenth of a milligram, since the deviations of the results show that the hundredths could have had no significance.

The extreme difference between the highest and the lowest values in the preliminary series is 0.33 unit, in the second series 0.09 unit, and in the third series 0.14 unit. At first sight these variations seem large, but their relative magnitude appears smaller when the great molecular weight of uranous bromide, 558.34, is taken into consideration. Thus the extreme percentage error of the preliminary series is 0.06, while those of the last two series are only 0.016 and 0.024 per cent respectively.

The so-called "probable error" of the average atomic weight computed from the six analyses numbered 7 to 12 inclusive, if each is given the same weight, is 0.015. That is, according to the theory of least squares, the atomic weight of uranium should be between 238.515 and 238.545.

The magnitude of the maximum deviations in these two final series is, moreover, about as large as would have been expected from known analytical uncertainty. The observed variation in the amount of sodic bromide, for which a constant correction had to be applied, would account for three quarters of it, and the rest, corresponding to less than the tenth of a milligram in the weighings, might easily be due to unavoidable errors of weighing or manipulation.

Further evidence of the trustworthiness of the figures is to be found in the comparison of the amounts of silver used in analyses 10, 11, and 12, with the corresponding amounts of argentic bromide, found in analyses 7, 8, and 9. This comparison is given in the following table, which gives the weights of silver corresponding to 100.000 parts of argentic bromide.

Weight of AgBr in vacuo.	Weight of Ag in vacuo.	Quotient × 100 = per cent of Silver in Argentic Bromide.
grams.	grams.	
2.42588	1.39365	57.449
1.43713	0.82259	57.447
2.50009	1.43617	57.445
	Average	57.447
	Stas found	57.445

The result not only verifies the mechanical work, but affords evidence that the precipitate must have been pure argentic bromide. Clearly, then, the analysis is as accurate as need be. Further repetition of the process might reduce the so-called "probable error," but could not change the average by a significant amount. In the present state of the question, the method seems to have been carried as far as expediency demands.

It is worth while to inquire whether or not the method may conceal some source of constant error beyond the reach of the experimental precautions detailed above. Such an error could hardly have occurred

during the analysis; for every step of this procedure was verified by confirmatory evidence. If a flaw existed, it must have been in the purity of the original substance. Since the observed atomic weight is lower than the former results, it is important to examine into only those possible irregularities which could have had the effect of lowering the apparent value.

The probable impurities tending to lower the atomic weight are, first, sodic bromide; second, hydrobromic acid; third, free bromine; fourth, uranic pentabromide; and fifth, an unknown metal with a lesser equivalent. The first impurity was found to be present, its amount was determined, and a suitable correction was applied. The second could not have been formed during the sublimation of the uranous bromide, because compounds of hydrogen were scrupulously excluded. If formed by the action of water after the sublimation, the atomic weight would have appeared too high — for moist uranous bromide emits hydrobromic acid instead of absorbing it. The third impurity, free bromine, could hardly have been imprisoned or absorbed by the sharply crystalline salt to any appreciable extent, since the concentration of the bromine vapor in the issuing gases was but small.

The evidence in regard to the absence of pentabromide is fairly conclusive, although somewhat indirect. All attempts by many investigators to form this compound have failed, in spite of the recognized existence of the corresponding chlorine compound. It seemed possible, however, that while this compound is not formed at high temperatures, lower temperatures might permit the addition of the extra bromine. Accordingly the preparations used in Analyses 7, 8, 10, and 11, were cooled in a current of dilute bromine vapor, instead of in pure nitrogen. The presence of a comparatively small amount of pentabromide would make a very decided difference in the quantity of bromine found. Hence the essential agreement of the average result of these analyses, 238.50, with the average result of all the others, 238.52, is good evidence of the absence of uranium pentabromide.

With regard to the fifth possible impurity nothing can be said except to point out the many operations involved in the purifications. These seem to point toward probable purity; but it is nevertheless to be regretted that lack of time prevented the analysis of many different fractions of material, prepared in varying ways.

The presence of oxybromide would of course cause low bromine analyses, and too high an apparent atomic weight. Therefore this possible cause of error need not be considered, even if the oxybromide had ever

been made in the absence of water. In the light of all these considerations, there would seem to be no good reason to question the purity of our bromide.

On comparing the result of this investigation, 238.53, with that of Zimmermann's, 239.59 (the only previous work worthy of serious consideration), the difference of over a unit seems at first to be one of great magnitude. The percentage difference (0.45%) is however smaller than many a difference which often has been passed by unheeded in small atomic weights, such as those of magnesium or aluminum. This point illustrates the difficulty of obtaining results with high atomic weights which can satisfy the cursory reader.

Nevertheless, such a difference is far too great to pass unchallenged. It seems highly probable that the greater part of it is due to the previously discussed sources of inaccuracy in Zimmermann's method, — especially to the difficulty of wholly re-oxidizing the lower oxide. The failure to oxidize half a per cent of the uranous oxide, involving an error in the weight of only 0.017 per cent of the total weight of the substance, would account for the discrepancy.

Hence it seems not unlikely that the atomic weight of uranium is really as low as 238.53. Nevertheless, the question cannot be looked upon as conclusively settled. Certainty can be obtained only by the application of a new method, radically different from the two just compared. Our experience of nearly four years of varied work seems to indicate that the search for such method will not be an easy one. The many degrees of quantivalence of uranium and the unsuitable properties of its compounds combine to render the problem one of unusual difficulty. When face to face with a problem of this kind one cannot but admire Stas's wisdom in selecting chiefly univalent elements with powerful affinities in order to prove the constancy of the atomic weights.

The result of our analyses of uranous bromide may be summed up in the following words: If oxygen is taken as 16.000, and bromine as 79.955, the atomic weight of uranium appears to be not far from 238.53.

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